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JAN 80 P M KUZNESOF , K J WYNNE , R S NOHR N00014-75-C-0693
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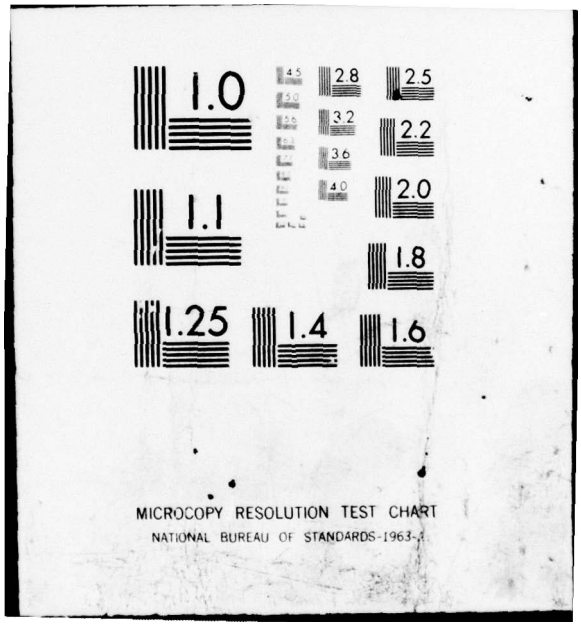
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Highly Conducting Iodinated Fluoroaluminum and Fluorogallium Phthalocyanine Polymers.

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SUMMARY

Partial oxidation of the quasi-one dimensional fluoroaluminum and fluorogallium phthalocyanines with iodine yields species with appreciable electrical conductivities (0.01-1 ohm^{-1} cm^{-1}); thermogravimetric, Raman spectroscopic, and mass spectrometric techniques have provided useful information about their compositions and nature.

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There is currently intense activity[2] aimed at the development of highly conducting organic and inorganic polymeric materials. Reports of greatly increased conductivity of oxosilicon and oxogermanium phthalocyanine polymers $(PcSiO)_x$ and $(PcGeO)_x$[3] when iodinated[2a] prompted us to examine the isoelectronic fluoroaluminum and fluorogallium phthalocyanine polymers $(PcAlF)_x$ and $(PcGaF)_x$.[4] Key interests were the conductivities of iodinated species and the evaluation of effects of ring separation and iodine/metal ratio on conductivity.

$(PcAlF)_x$ and $(PcGaF)_x$ were prepared by a route involving a template reaction between the respective metal trichlorides and phthalonitrile. The phthalocyanines thus formed were treated with base, aqueous hydrofluoric acid and pyridine, and then heated under vacuum at ~300°.[4,5] Vacuum sublimation of these fluorides (Al ~500°C, Ga ~460°C)gives mats of fine crystals. These crystals exhibit a needle-like habit, a strong dichroism (blue for light polarized perpendicular to the needle axis, colourless for light polarized parallel to the axis) and X-ray reflections in the 0.35 - 0.40 nm range which are strong and orientation dependent. Some crystals of the aluminum compound yield micrographs showing layer lattice lines parallel to the needle axis and spaced by ~1.4 nm. These data, together with the low solubility, low volatility, and low reactivity of the two fluorides, and the known propensity of aluminum and gallium for achieving octahedral coordination when possible, provide evidence that the fluorides are linear polymer analogs of $(PcSiO)_x$, $(PcGeO)_x$, and $(PcSnO)_x$.[3]

Iodinations of $(PcMF)_x$ were carried out at room temperature. One approach involved exposure of solid $(PcMF)_x$ to iodine vapor, using grease-free vacuum line techniques, until constant weight was attained (7-21 days). A second approach involved stirring a slurry of $(PcMF)_x$ in a solution of iodine in heptane until maximum iodination was achieved (~24 hr). In both cases, "maximum uptake" samples were generally divided into two portions. One portion was taken for immediate

analysis and characterization while the second portion was pumped on in vacuo to constant weight at room temperature to remove readily volatile iodine before being examined. The iodinated $(PcAlF)_x$ samples appear as fine, purple-black powders whereas the iodinated gallium derivatives range from magenta to purple-black. The undoped materials are blue-violet powders.

Compositions of the iodinated materials are presented in Table I along with room temperature conductivity data. Since the iodine content was sensitive to preparative conditions, it was essential to have a rapid and reliable analytical method for obtaining I/M ratios. Thermogravimetric analysis (TGA) proved to be a useful technique for this purpose, and in addition yielded valuable information on relative thermal stabilities. A characteristic thermogram was observed for "maximum uptake" compositions. Weight loss processes centered at about 80 and 180°C were observed. The onset of a major plateau at ~230°C signaled complete loss of iodine.[6] Above 230°C the thermograms follow those for the undoped materials which show weight loss beginning at >450°C. A low temperature (~80°C) loss of iodine is also observed for iodinated $(PcSiO)_x$, but the plateau corresponding to complete loss of iodine is reached at 340°. To demonstrate the analytical utility of TGA we note that for one iodinated PcAlF sample (Table 1, last entry) a 44% weight loss was recorded up to the plateau at ~230°), in agreement with an independent iodine weight uptake experiment which showed 43.1% iodine content. These percentages translate to an I/M ratio of 3.4 as noted in Table I.

As seen in Table I, striking increases in electrical conductivity 7,8 for both $(PcAlF)_x$ and $(PcGaF)_x$ result from their iodination. The largest increases, observed for highest iodine content, are 10^3 (Al) to 10^8 (Ga) greater than the

parent $(PcMF)_x$ compounds.[9] Also, for a comparable concentration of iodine, the conductivity of iodinated $(PcAlF)_x$ is greater than that of its gallium analog. These observations correlate with the closer inter-ring spacing for $(PcAlF)_x$.[4] This suggests that the conductive pathway involves significant π-π overlap between phthalocyanine rings.

Both Raman spectroscopy and iodine - 129 Mossbauer have been used to advantage for identification of the form(s) of iodine present in iodine-doped substances.[10,11] Initial Raman spectra of iodinated $(PcMF)_x$ (spinning discs, 514.5 nm excitation) show strong scattering attributable to I_3^-. (106-108 cm^{-1}) and I_5^- (164-168 cm^{-1}).[10,11] The expected overtones and combinations are also present. There was no evidence of I_2 scattering (ν - 180-210 cm^{-1}).[12,13]

The Raman data in combination with the TGA results suggest that initial loss of iodine (temperature invariant) arises from dissociation of I_5^- (and perhaps higher polyiodides). Complete loss of iodine due to triiodide decomposition and electron transfer back to the phthalocyanine polymer chain occurs at a higher temperature and is metal dependent (Al, Ga ~230°; (Si ~340°C). Supporting this view, the mass spectral profiles of I_2^+ intensity vs. temperature for $(PcAlF)_x$ and $(PcGaF)_x$ show two peaks between 30 and 300°C, consistent with the two-stage TGA weight loss. Significantly, the I_2^+ intensity vs. temperature profile of iodinated polyacetylene, $(CH)_x$, also exhibits a low and high temperature peak.[14]

This work makes it clear that oxidized fluorimetal phthalocyanine polymers constitute a new class of conducting polymers. In addition, the usefulness TGA for obtaining I/M ratios and relative thermal stabilities of iodine-doped conducting material has been demonstrated.

We thank Dr. F. J. Campbell and Mr. L. M. Johnson for use of their TGA, Dr. J. E. Reardon for use of the linear four-probe apparatus, Mr. P. G. Siebenman for van der Pauw conductivities, and Dr. J. R. Griffith for many stimulating discussions. We also thank the Office of Naval Research for partial support of this research.

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   b. Chemistry Program, Office of Naval Research, Arlington, VA 22217

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5. Satisfactory elemental analyses were obtained.

6. Mass spectral analysis reveals only loss of iodine below 300°. We thank Dr. William Allen for running the spectra.

7. Resistivities were calculated as described in L. B. Valdes, Proc. I.R.E., (1954) 42, 420.

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9. The high conductivity (6×10^{-4} $ohm^{-1}cm^{-1}$) of $(PcAlF)_x$ is probably due to impurities; the conductivity drops to 6×10^{-9} $ohm^{-1}cm^{-1}$ at 133K.

10. Variable temperature-conductivity data for iodinated samples are in the process of being collected.

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Table I. Compositions and Conductivities[a] for Iodinated $(PcAlF)_x$ and $(PcGaF)_x$

I/Al	σ (ohm^{-1} cm^{-1})	I/Ga	σ (ohm^{-1} cm^{-1})
0	1.5×10^{-4}[b]	0	$< 10^{-6}$[b]
0.21[c,f]	1.8×10^{-2}	0.17[d,f]	1.9×10^{-4}
0.29[d,f]	1.5×10^{-2}	0.62[c,f]	1.7×10^{-2}
0.38[c,f]	2.0×10^{-2}	0.77[d,e]	4.4×10^{-2}
0.87[d,f,h]	0.70	0.97[f,d]	7.2×10^{-2}
1.0[d,e]	0.13	0.98[e,g]	8.6×10^{-2}
1.5[e,g]	0.19	2.3[f,g]	0.15
2.4[d,f]	0.63		
3.4[f,g]	0.59		

[a] Room temperature, linear four-probe technique, pressed pellets.

[b] Conductivities obtained using the four-probe van der Pauw method were 6.3×10^{-4} and 6.5×10^{-9} ohm^{-1} cm^{-1} at 300K and 133K, respectively, for $(PcAlF)_x$ and 8.2×10^{-10} ohm^{-1} cm^{-1} at 300K for $(PcGaF)_x$.

[c] Iodine uptake interrupted before maximum weight gain reached.

[d] Pumped on in vacuo to constant weight.

[e] Heptane slurry reaction.

[f] Solid-vapor reaction in vacuo.

[g] Maximum iodine uptake.

[h] $(PcAlF)_x$ purified by sublimation was used.

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